



Short communication

Improved Zn/Zn(II) redox kinetics, reversibility and cyclability in 1-ethyl-3-methylimidazolium dicyanamide with water and dimethyl sulfoxide added

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HIGHLIGHTS

- H₂O enhances the conductivity of 1-ethyl-3-methylimidazolium dicyanamide (EMI-DCA).
- Adding H₂O to EMI-DCA improves Zn redox kinetics.
- Adding dimethyl sulfoxide (DMSO) to EMI-DCA maintains Zn redox cyclability.
- EMI-DCA + H₂O + DMSO (mole ratio = 1:1:2.3) optimizes Zn/Zn(II) redox performance.

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ABSTRACT

Diluents composed of H₂O and dimethyl sulfoxide (DMSO) were added to 1-ethyl-3-methylimidazolium dicyanamide (EMI-DCA), yielding an electrolyte system that is potentially applicable for Zn-air batteries. H₂O is critical for enhancing both the electrolyte conductivity and Zn/Zn(II) redox kinetics, but impairs Zn/Zn(II) redox reversibility and cyclability. DMSO has the ability to stabilize the electrolyte from H₂O decomposition and is beneficial for maintaining Zn/Zn(II) redox reversibility and cyclability. Improved Zn/Zn(II) redox kinetics and reversibility, together with good cyclability up to 200 cycles, was achieved in EMI-DCA + H₂O + DMSO in a mole ratio of 1:1:2.3.

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1. Introduction

Characterized by negligible volatility and a wide electrochemical window (~3 V), 1-ethyl-3-methylimidazolium dicyanamide (EMI-DCA) is a promising room temperature ionic liquid (RTIL) to replace conventional aqueous electrolytes for Zn-air batteries, where electrolyte “drying out” could be prevented. EMI-DCA also stands out with its relatively high conductivity (~25 mS cm⁻¹) among RTILs, which typically have conductivities less than 10 mS cm⁻¹. With respect to Zn electrochemistry, our previous work [1] showed that Zn/Zn(II) redox has a high current density in RTILs with [EMI]⁺ cations and a small reaction overpotential, specifically with [DCA]⁻ anions, suggesting that desirable

Zn redox behavior could be achieved in EMI-DCA. Moreover, electrodeposition of non-dendritic and compact Zn films was obtained in EMI-DCA [2], which is preferred in Zn-air batteries to avoid short-circuit issues.

The strategy of introducing H₂O into RTILs has proven to be an effective way to improve electrolyte conductivity and Zn redox kinetics [3,4]. Compared with H₂O, dimethyl sulfoxide (DMSO) has a slightly higher viscosity but a lower vapor pressure [5], so as a diluent for RTILs it may be able to increase their conductivity while maintaining low volatility. As a polar solvent, DMSO also facilitates the solvation of Zn(II) ions [6] and is capable of stabilizing oxygen reduction reaction intermediates (superoxide radical) [7]. All these features make DMSO a potentially good additive in RTILs for Zn-air battery applications. To the authors' knowledge, this is the first study to propose adding H₂O and DMSO as diluents, to optimize the electrochemical system for the benefit of Zn/Zn(II) electrochemical behavior in EMI-DCA.

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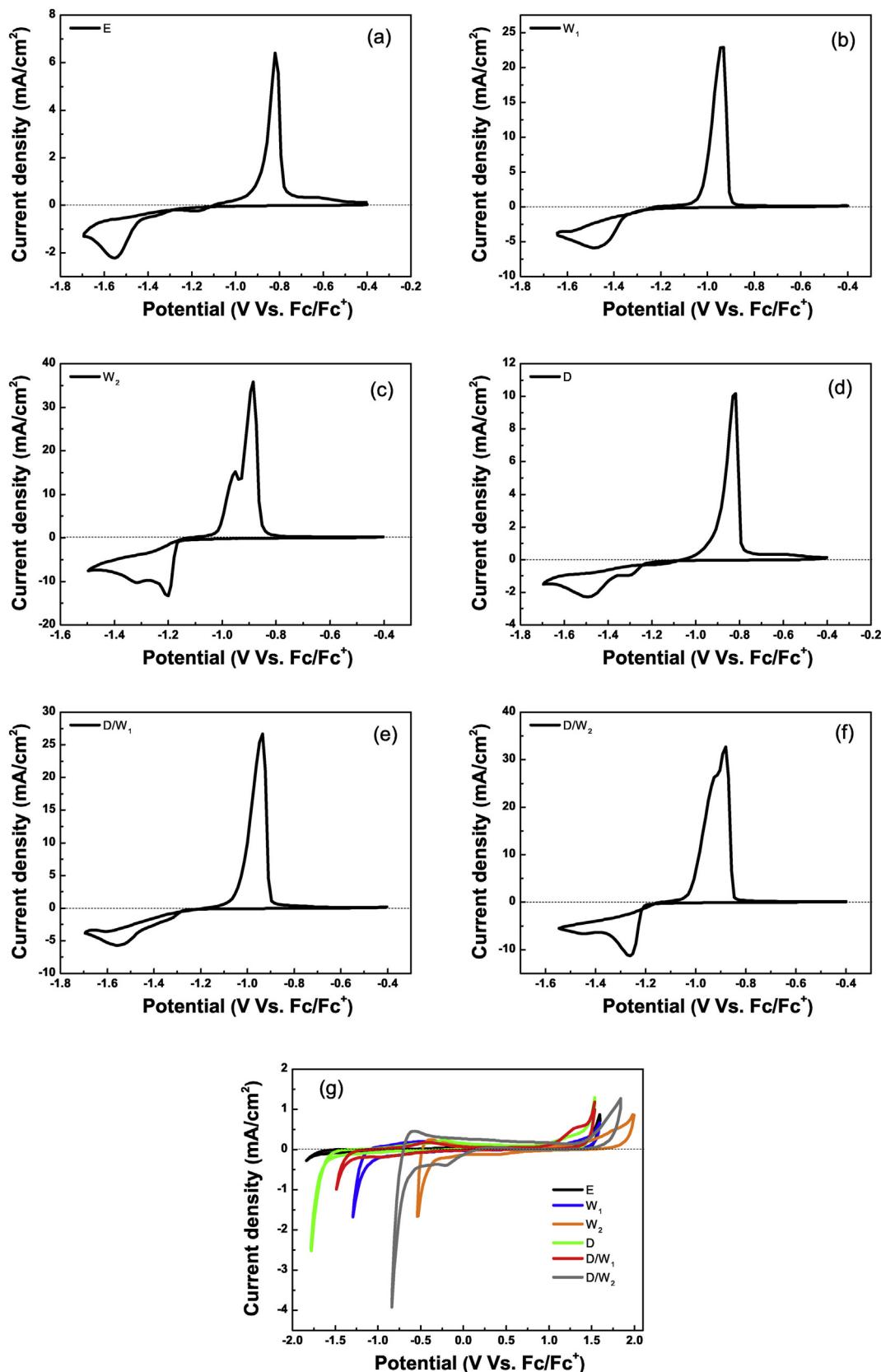


Fig. 1. Cyclic voltammetry plots at 50 mV s⁻¹ for Zn/Zn(II) redox in EMI-DCA based electrolytes: (a) E: EMI-DCA; (b) W₁: EMI-DCA + H₂O (1:1.1); (c) W₂: EMI-DCA + H₂O (1:6.6); (d) D: EMI-DCA + DMSO (1:2.3); (e) D/W₁: EMI-DCA + H₂O + DMSO (1:1.1:2.3); (f) D/W₂: EMI-DCA + H₂O + DMSO (1:6.6:2.3); (g) electrochemical window for each electrolyte in the absence of Zn(II) ions.

This paper presents the findings based on using H₂O and DMSO to modify EMI-DCA based electrolytes that are potentially applicable for Zn–air batteries. Applying cyclic voltammetry, chronoamperometry and potentiodynamic polarization, the effects of H₂O and/or DMSO addition on the kinetics, reversibility and cyclability of Zn/Zn(II) redox behavior are investigated. The morphology and composition of deposits remaining on the working electrode after cycling are observed and analyzed using scanning electron microscopy (SEM) and X-ray diffraction (XRD), with the purpose of shedding some light on the products of electrode reactions. The amount of H₂O and DMSO addition was based on optimization of conductivity, which is not presented here. A mole ratio of EMI-DCA (~25 mS cm⁻¹) to H₂O of 1:6.6 and EMI-DCA to DMSO of 1:2.3 correspond to the highest measured electrolyte conductivities of ~70 mS cm⁻¹ and ~30 mS cm⁻¹, respectively. EMI-DCA with H₂O at a mole ratio of 1:1.1 shows a doubled conductivity of ~50 mS cm⁻¹.

2. Experimental

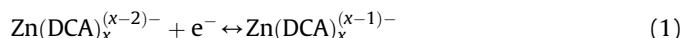
EMI-DCA (C₈H₁₁N₅ >98 wt%, with <0.2 wt% H₂O and <1.5 wt% halides) was purchased from IoLiTec and Zn bis(trifluoromethanesulfonyl)imide (Zn–TFSI, 99 wt%) was purchased from Solvionic. The chemicals were used as received without further treatment. Electrolytes were prepared by first vacuum drying EMI-DCA at ~90 °C overnight and then diluting with deionized H₂O (18.2 MΩ cm) and/or DMSO (100%, Fisher Scientific). Zn–TFSI was dissolved in each electrolyte by stirring overnight under ambient temperature to produce a 0.1 mol l⁻¹ Zn(II) solution for electrochemical measurements.

A Zahner IM6 electrochemical workstation (controlled by Thales 4.15 software) and a BASi system (Bioanalytical Systems, Inc.) were applied to perform electrochemical tests. Cyclic voltammetry (CV) at 50 mV s⁻¹ was undertaken within the range of -1.7 to -0.4 V and -1.85 to 2 V vs. Fc/Fc⁺ for studying Zn/Zn(II) redox reactions and the electrochemical window of each electrolyte, respectively. Two hundred cycles were also applied in CV tests at 10 mV s⁻¹ to explore Zn/Zn(II) redox cyclability. Chronoamperometry experiments were accomplished by stepping the potential of the working electrode from open circuit potential to -1.5 to -1.7 V vs. Fc/Fc⁺, where the reduction of the Zn species is a diffusion-controlled process. Potentiodynamic polarization experiments were performed at 1 mV s⁻¹. All electrochemical experiments used a 3-electrode cell configuration, consisting of a 1.6 mm diameter Pt (MF-2013 BASi) working electrode (WE), a 0.5 mm diameter Pt wire (MW-1032 BASi) counter electrode (CE) and a reference electrode (RE), which was assembled with a Pt wire inserted in a glass tube filled with EMI-DCA containing 50:50 mol% Fc/Fc⁺ as the internal potential standard with the addition of H₂O at the same concentration as that of the studied electrolytes. The inner solution of the RE was separated from the studied electrolyte by a porous Vycor tip (MF-2042 BASi).

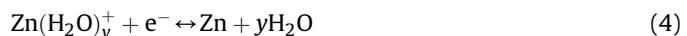
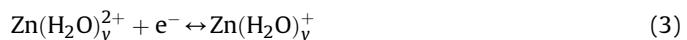
To study the morphology of deposits after a 200 cycle CV test, a 3-electrode cell configuration was also applied, with the same RE as for the electrochemical measurements, a Pt coated Si substrate as the WE and a Zn plate as the counter electrode placed vertically within 20 mm from the WE. After CV cycling, the substrate was thoroughly rinsed with acetone, ethanol and dried in air. The morphology of the deposit was analyzed with a Hitachi S-4700 scanning electron microscope (SEM) operated at 15 kV. Low voltage (0.8–1.0 kV) secondary electron (SE) imaging was also applied to distinguish Zn from the oxidation product ZnO, which may be present in deposited films. The phases present in the deposited films were confirmed through XRD analysis, using a Bruker D8 X-ray diffractometer. The diffractometer was operated in thin film mode with the incident beam at a glancing angle of 0.5° to the sample surface, in order to minimize the XRD signal from the substrate.

3. Results and discussion

Typical CV curves for Zn/Zn(II) redox in the studied electrolytes are compared in Fig. 1. In electrolytes with no H₂O (Fig. 1(a) and (d)), two reduction peaks are notable in the CV curves, indicating that Zn(II) ions are reduced to Zn in two steps via receiving one electron per step. This is attributed to the complexing ability of [DCA]^{x-} anions towards Zn(II) ions to form complex ions, Zn(DCA)_x^{(x-2)-}. Potentials for the first and second reduction step range from -1.3 to -1.35 V and -1.5 to -1.55 V, respectively. The corresponding electrode reactions during reduction are proposed as follows:



The same reaction mechanism has been discussed in our previous study on Zn redox in BMP-DCA (1-butyl-1-methylpyrrolidinium dicyanamide), an ionic liquid with the same anion [1]. In electrolytes with H₂O added (Fig. 1(b), (c), (e) and (f)), Zn(II) ions are likely to coordinate with either H₂O or [DCA]^{x-} anions to form both Zn(H₂O)_y²⁺ and Zn(DCA)_x^{(x-2)-} complex ions. Compared with Zn(DCA)_x^{(x-2)-}, Zn(H₂O)_y²⁺ ions are smaller in size and diffuse easier. As seen in Table 1, the diffusion coefficient for the Zn species increases with water concentration, reflecting the increased ratio of Zn(H₂O)_y²⁺ to Zn(DCA)_x^{(x-2)-} ions. It is also notable that in EMI-DCA + H₂O (1:6.6) and EMI-DCA + H₂O + DMSO (1:6.6:2.3), the diffusion coefficients are one order of magnitude higher than the others. This implies that Zn(H₂O)_y²⁺ ions occupy a high ratio in the complex ions, and compete with Zn(DCA)_x^{(x-2)-} ions for involvement in the reduction reactions. Consequently, in addition to reactions (1) and (2), reactions (3) and (4) can also take place and even prevail as the positive Zn(H₂O)_y²⁺ ions are more readily attracted to the electrode surface with excess electrons than Zn(DCA)_x^{(x-2)-} ions with negative charge:



As can be seen in Fig. 1(c) and (f), the resultant peak potentials for Zn(II) reduction in EMI-DCA + H₂O (1:6.6) and EMI-DCA + H₂O + DMSO (1:6.6:2.3) shift to more positive positions, i.e., -1.2 to -1.25 V and -1.35 to -1.45 V, compared with that in EMI-DCA without additions or with DMSO addition only (Fig. 1(a))

Table 1
Electrochemical behavior of Zn/Zn(II) redox in EMI-DCA based electrolytes.

Electrolyte	D ₀ ^a (×10 ⁻⁶ cm ² s ⁻¹)	j ₀ ^b (mA cm ⁻²)	ΔE _p ^c (V)	Q _a /Q _c ^d at CV cycle 2	Q _a /Q _c at cycle 200
E	0.10	0.0016	0.73	0.84	0.85
W ₁	0.90	0.014	0.58	0.62	0.11
W ₂	6.00	0.12	0.36	0.59	0.07
D	0.30	0.0089	0.67	0.89	0.80
D/W ₁	0.80	0.032	0.57	0.91	0.89
D/W ₂	8.80	0.13	0.41	0.84	0.15

^a Diffusion coefficient.

^b Exchange current density.

^c Peak potential separation.

^d Ratio of Q_a to Q_c (Q_c is the charge integrated for Zn reduction and Q_a is the charge integrated for Zn oxidation).

(E: EMI-DCA; W₁: EMI-DCA + H₂O (1:1.1); W₂: EMI-DCA + H₂O (1:6.6); D: EMI-DCA + DMSO (1:2.3); D/W₁: EMI-DCA + H₂O + DMSO (1:1.1:2.3); D/W₂: EMI-DCA + H₂O + DMSO (1:6.6:2.3)).

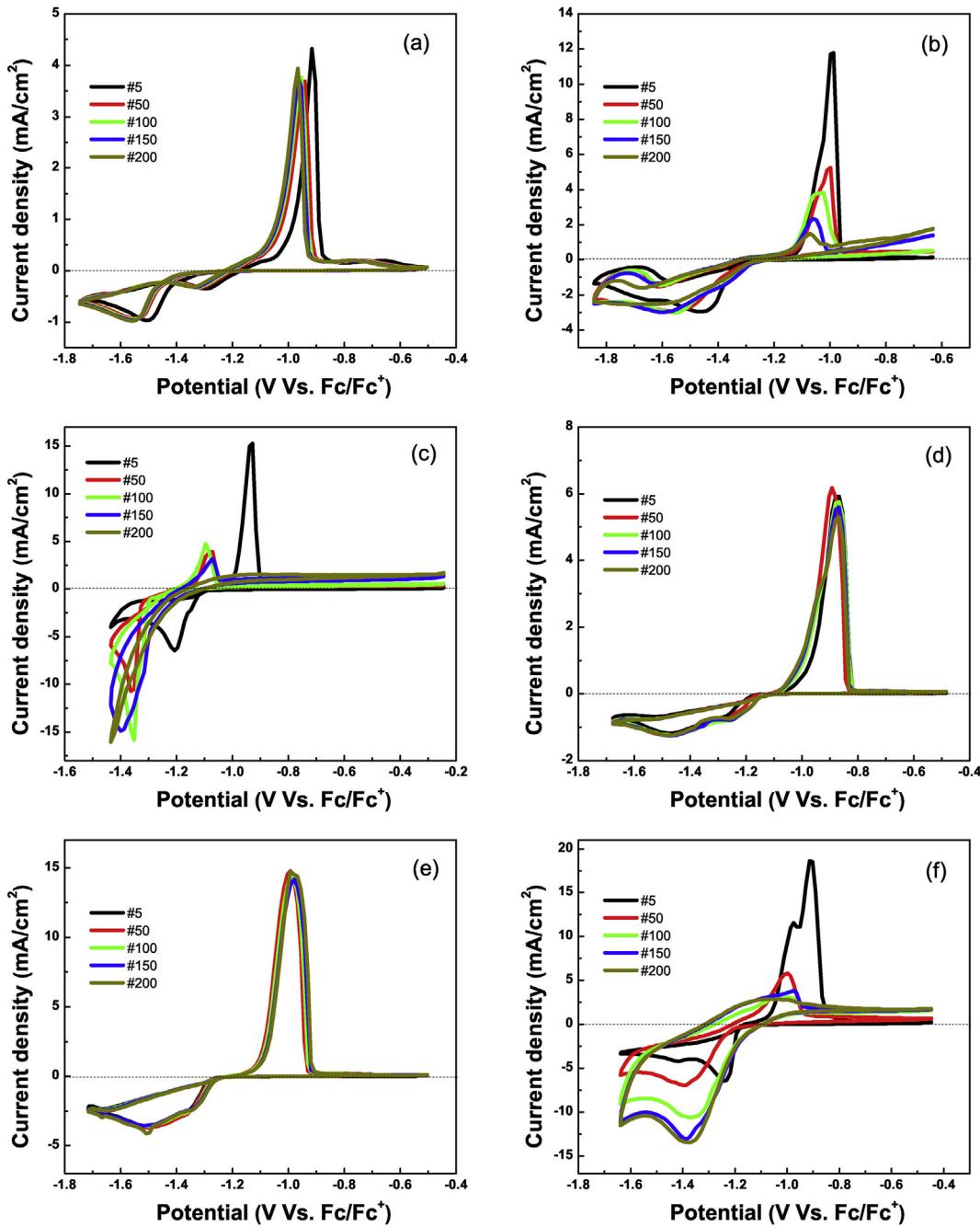


Fig. 2. Cyclability of Zn/Zn(II) redox in EMI-DCA based electrolytes at 10 mV s⁻¹: (a) E: EMI-DCA; (b) W₁: EMI-DCA + H₂O (1:1.1); (c) W₂: EMI-DCA + H₂O (1:6.6); (d) D: EMI-DCA + DMSO (1:2.3); (e) D/W₁: EMI-DCA + H₂O + DMSO (1:1.1:2.3); (f) D/W₂: EMI-DCA + H₂O + DMSO (1:6.6:2.3) ("#" denotes the cycle number).

and (d)). For electrolytes EMI-DCA + H₂O (1:1.1) and EMI-DCA + H₂O + DMSO (1:1.1:2.3), with relatively small amounts of water, Zn(DCA)_x^{(x-2)-} remains as the dominant complexing ion involved into the electrode reactions, with their peak reduction potentials being similar to that observed for EMI-DCA without additions or with DMSO addition only. It is worth noting that a higher overpotential is required for Zn deposition in ionic liquids compared with traditional zincate aqueous electrolytes. In the latter case, Zn reduction is coupled with hydrogen evolution [8]. The adsorbed hydrogen atoms react with the Zn(II) species, yielding a low overpotential for zinc deposition [9].

As shown in Table 1, H₂O plays a leading role in improving the Zn/Zn(II) redox kinetics, including increasing the diffusion rate and

the exchange current density, as well as decreasing the overpotential (peak potential separation). With regard to Zn/Zn(II) redox reversibility, as evaluated by the ratio of Q_a/Q_c, Zn/Zn(II) redox exhibits superior reversibility in EMI-DCA with DMSO. Q_c is the charge integrated for Zn reduction and Q_a is the charge integrated for Zn oxidation; the closer Q_a/Q_c is to 1, the better the reversibility. Adding H₂O only to EMI-DCA impairs Zn/Zn(II) redox reversibility, while the addition of both H₂O and DMSO maintains good reversibility. By examining the electrochemical window (EW) of each electrolyte (Fig. 1(g)), it is found that adding DMSO has a negligible effect on the EW of EMI-DCA, but the EW can be severely reduced with the addition of H₂O. The decomposition of H₂O molecules may account for the sharp increase in cathodic current

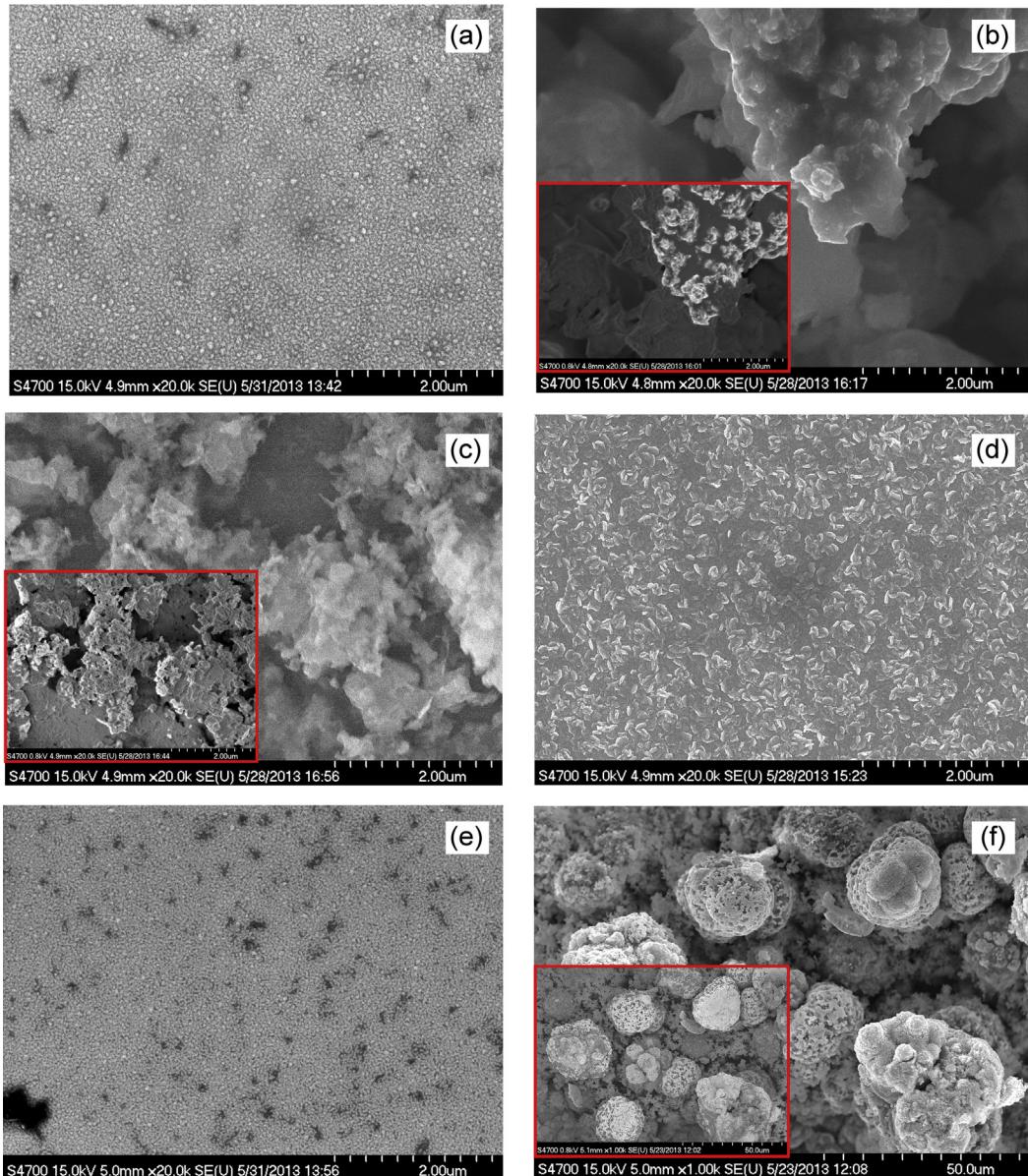


Fig. 3. SEM secondary electron (SE) images of deposits on the substrate surface after cycling for 200 cycles in EMI-DCA based electrolytes: (a) E: EMI-DCA; (b) W₁: EMI-DCA + H₂O (1:1:1); (c) W₂: EMI-DCA + H₂O (1:6:6); (d) D: EMI-DCA + DMSO (1:2:3); (e) D/W₁: EMI-DCA + H₂O + DMSO (1:1:1:2:3); (f) D/W₂: EMI-DCA + H₂O + DMSO (1:6:6:2:3). Inset images in b, c and f are taken at the same location with a lower accelerating voltage of 0.8 kV; darker regions are ZnO and lighter contrast regions are Zn.

density observed in Fig. 1(g) at -1.3 V and -0.5 V in EMI-DCA + H₂O (1:1:1) and EMI-DCA + H₂O (1:6:6), respectively. DMSO seems to have the ability of stabilizing H₂O molecules (probably through H-bonding), resulting in a slightly wider EW for EMI-DCA added with both H₂O and DMSO than that with H₂O as the only additive.

The cyclability of Zn/Zn(II) redox was further examined and the evolution of CV scans with cycle number is shown in Fig. 2. As expected, in electrolytes EMI-DCA, EMI-DCA + DMSO (1:2:3) and EMI-DCA + H₂O + DMSO (1:1:1:2:3) (Fig. 2(a), (d) and (e)), Zn/Zn(II) redox maintains good reversibility after 200 cycles as reflected by the high ratio of $Q_a/Q_c (>0.8)$, Table 1 and shows negligible shift in potential, exhibiting desirable cyclability. On the other hand, Zn/Zn(II) gradually loses its reversibility with cycle number and shows poor cyclability in the other three electrolytes with H₂O addition. Particularly in EMI-DCA with H₂O in a high concentration (Fig. 2(c) and (f)), with cycling, the peak reduction potential shifts from about -1.2 to -1.25 V to more negative positions around -1.35

to -1.4 V. This is most likely because of decreasing amounts of $Zn(H_2O)_2^{2+}$ ions being involved in the electrode reactions due to the decomposition of H₂O molecules during cycling. It is also notable that the oxidation peaks in Fig. 2(b), (c) and (f) gradually disappear with cycling. Water decomposition produces OH⁻ ions, which could further react with Zn²⁺ ions and lead to the formation of ZnO. Therefore, the reduction peaks observed in Fig. 2(b), (c) and (f) could be due to the formation of ZnO, which hinders the reduction of Zn²⁺ ions and leads to diminishing Zn oxidation peaks observed during the reverse scan. In order to confirm this hypothesis, the morphology of the deposits that remained on the substrate surface after cycling was examined and is presented in Fig. 3. From electrolytes EMI-DCA, EMI-DCA + DMSO (1:2:3) and EMI-DCA + H₂O + DMSO (1:1:1:2:3) (Fig. 3(a), (d) and (e)), nanoscale Zn deposits (approximately hundreds of nanometers thick) are present on the substrate after the last CV cycle was concluded on the oxidation side. This kind of morphology demonstrates that Zn

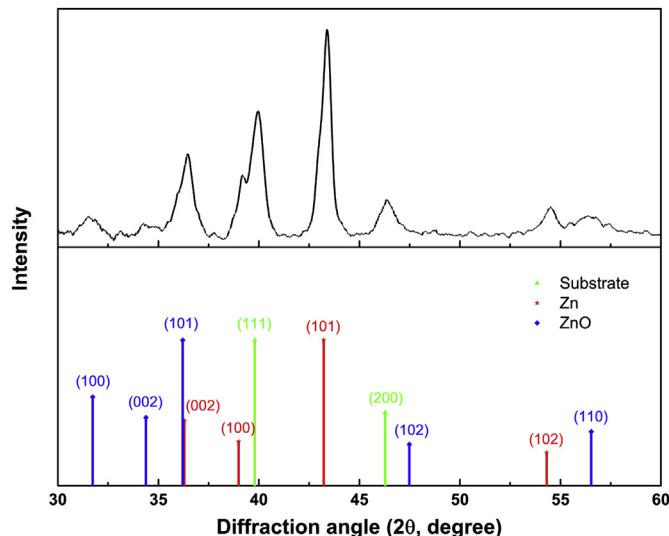


Fig. 4. XRD pattern for the deposit after 200 cycles in electrolyte W_1 : EMI-DCA + H_2O (1:1.1).

deposits which form during the reduction process are mostly oxidized/dissolved back into the electrolyte during the reverse scan. This is an indication of good reversibility and cyclability for Zn/Zn(II) redox as predicted from the CV results. On the contrary, after 200 CV cycles, thicker deposits (on the micron scale) remain on the substrate from electrolytes EMI-DCA + H_2O (1:1.1), EMI-DCA + H_2O (1:6.6) and EMI-DCA + H_2O + DMSO (1:6.6:2.3), indicating the poor reversibility for Zn/Zn(II) redox reactions. As seen in Fig. 3(b), (c) and (f), the porosity of these deposits is obvious, suggesting the presence of ZnO. SEM images for these samples were taken at low accelerating voltages (0.8 kV) to reveal the contrast difference between Zn (brighter regions) and ZnO (darker regions); these images are shown as insets in Fig. 3(b), (c) and (f). The secondary electron (SE) yield for Zn increases significantly at lower voltages, while the SE yield for ZnO varies little with changing voltage, which produces the contrast. The detailed contrast mechanism for distinguishing between ZnO and Zn is discussed in Ref. [10]. A representative XRD pattern for one of these samples, i.e., EMI-DCA + H_2O (1:1.1), is shown in Fig. 4; the other samples had similar patterns. Both Zn and ZnO are clearly identified in the thin film, which confirms the SEM observation. Therefore, the formation of ZnO in EMI-DCA + H_2O (1:1.1), EMI-DCA + H_2O (1:6.6) and EMI-DCA + H_2O + DMSO (1:6.6:2.3) during CV cycling is confirmed through both SEM imaging and XRD structural analysis.

For Zn–air battery applications, any potential electrolyte should exhibit high conductivity and, equally important, balanced electrochemical behavior for Zn/Zn(II) redox reactions. Adding H_2O as a diluent to EMI-DCA is effective in enhancing both the electrolyte conductivity and Zn/Zn(II) redox kinetics, with a trade-off of decreased Zn/Zn(II) redox reversibility and cyclability. Based on the current study, the drawbacks brought on by H_2O addition can be compensated somewhat by adding DMSO as a supplementary diluent. The addition of mixed diluents, e.g., H_2O and DMSO, at the correct composition to EMI-DCA (EMI-DCA + H_2O + DMSO (1:1.1:2.3)) generates a desirable electrolyte system. There is potential to fabricate batteries with high energy density and good cycle life, as indicated by the achievement of high kinetics, desirable reversibility and cyclability for Zn/Zn(II) redox.

4. Conclusions

Adding both H_2O and DMSO to EMI-DCA leads to a synergistic effect that improves the electrochemical performance of the Zn/Zn(II) redox reaction, in terms of reversibility and kinetics, that is not achievable with H_2O or DMSO alone. For mixed diluent systems, a large amount of H_2O addition impairs both Zn/Zn(II) redox reversibility and cyclability. However, an electrolyte with EMI-DCA + H_2O + DMSO in a mole ratio of 1:1.1:2.3 is favorable in terms of guaranteeing improved kinetics, reversibility and cyclability for Zn/Zn(II) redox.

Acknowledgments

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